DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 56

TENNESSEE PHOSPHATE ROCK

[All results are based on a sample dried for one hour at 105° C.]

ANALYSTS*	TOTAL P_2O_5		Total Fe_2O_3	Total Al_2O_3	Total CaO	Insoluble P_2O_5 after aqua regia attack
	Gravimetric method	Alkalimetric method				
1	31.31	31.29	3.30	3.07	44.8	0.02
2	31.33	31.39				
Averages	31.32	31.34	3.30	3.07	44.8	.02
General averages	31.33		3.30	3.07	44.8	.02

Less carefully made analyses gave: Matter insoluble in concentrated hydrochloric acid 8.04 per cent; silica (with no regard to fluorides present), 6.72 per cent; titania (TiO_2), 0.15 per cent; manganese oxide (MnO), 0.25 per cent; total sulphur (as SO_3), 2.70 per cent; sulphur as SO_3 (soluble in 1 : 1 hydrochloric acid), 1.23 per cent; total MgO, 0.40 per cent; copper (as CuO), less than 0.003 per cent; arsenic (as As_2O_5) less than 0.005 per cent; CO_2, 2.0 per cent; fluorine, 2.6 per cent, K_2O, 0.6 per cent, and Na_2O, 1.1 per cent.

"Soluble Iron."—Very concordant results were obtained for "soluble iron" by the method recommended by the Fertilizer Division of the American Chemical Society, J. Ind. Eng. Chem., 7, pp. 447–448; 1915; *provided* the precaution concerning carbonaceous matter was observed. The general average was 2.55 per cent Fe_2O_3. The details of the method for "soluble iron" are given on the following pages.

"Soluble Alumina."—Concordant results were not obtained for "soluble alumina" by the method recommended in the reference given above. The results varied from 3.09 to 3.28 per cent Al_2O_3 and indicated more "soluble alumina" than the total alumina content of the sample. The result 2.81 per cent Al_2O_3 was obtained by the method for "soluble alumina" described on the following pages.

*LIST OF ANALYSTS

1. James I. Hoffman, Bureau of Standards. | 2. H. B. Knowles, Bureau of Standards.

George K. Burgess
Director.

Washington, D. C.
May 20, 1927.

METHODS OF ANALYSIS

DRYING

Dry for one hour at 105° C. in a well-ventilated oven.

DETERMINATION OF PHOSPHORIC ACID (P_2O_5)

SOLUTION OF THE SAMPLE

Transfer 2.5 g of the 80-mesh rock to a 400 cc beaker, add 30 cc of hydrochloric acid (sp. gr. 1.19) and 10 cc of nitric acid (sp. gr. 1.42) and boil to a sirupy consistency. Add 1 g of boric acid and dissolve the residue, which should be nearly solid after cooling, in 5 cc of concentrated nitric acid and 50 cc of water. Heat to boiling, cool, filter into a 250 cc graduated flask, wash the filter thoroughly with cold water, and dilute to the mark. This procedure eliminates practically all of the silica, but it is necessary to filter soon after digestion in order to prevent resolution of some of it.

GRAVIMETRIC METHOD

Solutions required.—*Molybdate solution.*—Mix 100 g of pure molybdic anhydride or 118 g of 85 per cent molybdic acid with 400 cc of water and add 80 cc of ammonium hydroxide (sp. gr. 0.90). When solution is complete, filter and pour the solution slowly and with constant stirring into a mixture of 400 cc of nitric acid (sp. gr. 1.42), and 600 cc of water. Let settle for 24 hours and use the clear supernatant liquid.

Ammonium nitrate solution (5 per cent).—Dissolve 50 g of ammonium nitrate in 950 cc of water.

Ammonium hydroxide—ammonium citrate solution.—Dissolve 25 g of citric acid in 700 cc of water and add 350 cc of ammonium hydroxide (sp. gr. 0.90).

Dilute ammonium hydroxide (1 : 20).—Mix 50 cc of ammonium hydroxide (sp. gr. 0.90) and 1,000 cc of water.

Dilute hydrochloric acid (1 : 20).—Mix 50 cc of hydrochloric acid (sp. gr. 1.19) and 1,000 cc of water.

Magnesia mixture.—Dissolve 50 g of $MgCl_2 . 6H_2O$ and 100 g of NH_4Cl in 500 cc of water. Add ammonium hydroxide in slight excess, let stand overnight, and filter if a precipitate appears. Make barely acid with hydrochloric acid and dilute to 1,000 cc.

Procedure.—Transfer a 50 cc aliquot portion of the prepared solution (representing 0.5 g of the rock) to a 250 or 300 cc Erlenmeyer flask, add 15 cc of nitric acid (sp. gr. 1.42), and nearly neutralize with ammonium hydroxide (sp. gr. 0.90). Add 125 cc of ammonium molybdate solution and digest at 60° C. for 30 minutes with frequent stirring or shaking. Cool by immersing in tap water for five minutes, filter on a paper of close texture, keep as much of the precipitate as possible in the flask, and wash the flask and the precipitate five times with a 5 per cent solution of ammonium nitrate. Set the filtrate and washings aside after thorough mixing and make sure that no further separation of phosphomolybdate occurs.

Dissolve the precipitate in the flask in 20 cc of ammonium hydroxide-ammonium citrate solution. Pour this solution through the filter which contains the remainder of the yellow precipitate and catch the solution in a 250 cc beaker. Wash the flask and paper several times with a dilute solution of ammonium hydroxide (1 : 20), next with a little hot water, and finally with hot dilute hydrochloric acid (1 : 20). The volume of the solution at this point should be between 100 and 150 cc. Neutralize the ammoniacal solution with hydrochloric acid, using litmus as indicator, and add 1 cc of hydrochloric acid, (sp. gr. 1.19) and 10 cc of magnesia mixture per decigram of phosphorus pentoxide (P_2O_5). Now add ammonium hydroxide (sp. gr. 0.90) dropwise and with continuous stirring until the solution is ammoniacal and most of the phosphorus has been precipitated. Finally add 15 cc more of ammonium hydroxide and allow the solution to stand for 4 hours or overnight at room temperature. The time of standing may be reduced to 2 hours if the solution is kept in a refrigerator or an ice-water bath. Filter and wash the magnesium-ammonium phosphate precipitate several times with dilute ammonium hydroxide (1 : 20), and dissolve it on the filter in 25 cc of dilute hydrochloric acid (1 : 1), catching the solution in the original beaker containing the bulk of the precipitate. Wash the filter thoroughly with dilute hydrochloric acid (1 : 20) and dilute the solution to 100 cc. Add 2 to 3 cc of magnesia mixture and then ammonium hydroxide slowly until a crystalline precipitate appears, and finally an excess of 3 to 5 per cent by volume. Allow to stand as before. Transfer the precipitate to a 9 cm Whatman No. 42 filter or its equivalent and wash with dilute ammonium hydroxide (1 : 20). Ignite the precipitate carefully and at as low a temperature as possible until the carbon has been destroyed. Finally ignite at approximately 1,000° C. to constant weight, and calculate to P_2O_5 by multiplying the weight of $Mg_2P_2O_7$ by 0.6379.

ALKALIMETRIC METHOD

Solutions required.—*Ammonium hydroxide (sp. gr. 0.96, or approximately 6 N).*—Mix 400 cc of ammonium hydroxide (sp. gr. 0.90) with 600 cc of water. This solution should be checked with a hydrometer or by titration.

Potassium nitrate solution (1 per cent).—Dissolve 10 g of potassium nitrate in 1,000 cc of water.

Standard sodium hydroxide solution (approximately 0.3 N).—Prepare a saturated solution of sodium hydroxide in a stoppered flask, let settle overnight, and pipet a clear 20 cc portion. Dilute to 1,000 cc with recently boiled water, cool to room temperature, and standardize against the Bureau of Standards Standard Benzoic Acid No. 39c or Acid Potassium Phthalate No. 84. Dilute, if desirable, restandardize, and protect the solution from carbon dioxide. The P_2O_5 titre should be calculated from the ratio 1 P_2O_5 : 46 NaOH, and the titre of the solution checked against phosphate rock of known P_2O_5 content.

Standard nitric acid solution (approximately 0.3 N).—Mix 20 cc of nitric acid (sp. gr. 1.42) and 1,000 cc of water, cool to room temperature, and standardize against the standard sodium hydroxide solution. Adjust the solution until it is exact equivalent.

Phenolphthalein solution (1 per cent).—Dissolve 1 g of pure phenolphthalein in 100 cc of 85 to 95 per cent alcohol.

Procedure.—Transfer a 10 cc or a 25 cc portion of the prepared solution to a 300 cc Erlenmeyer flask, add 25 cc of nitric acid (sp. gr. 1.42), and dilute to [illegible]0 cc. Add to the solution 40 cc of ammonium hy[illegible]oxide (sp. gr. 0.96) and 50 cc of ammonium molybdate solution, shake for 10 minutes, and let stand for 20 minutes. Filter on an 11 cm paper of close texture, wash the flask and precipitate five times with 15 to 20 cc portions of a 1 per cent solution of potassium nitrate; then wash the filter paper containing the most of the precipitate five times with like portions of the same solution (about 200 cc of wash solution in all). The paper, should, of course, be carefully washed each time from the rim downwards and then allowed to drain completely before washing with the next portion of solution. The wash solution, as well as all others subsequently used, must be free from carbon dioxide. Return the paper and precipitate to the flask, add enough 0.3 *N* sodium hydroxide to decompose the precipitate and then approximately 2 cc in excess. Dilute with 25 cc of water, stopper, and shake until the precipitate is dissolved. Dilute to approximately 150 cc with water, add 6 drops of a 1 per cent solution of phenolphthalein, and discharge the pink color with standard acid. Finish the titration by adding standard alkali until the reappearance of the pink color. Subtract the volume of acid used from the *total* volume of alkali and multiply the remainder by the titre of the alkali solution.

DETERMINATION OF SOLUBLE IRON AND ALUMINA

Solutions required.—*Hydrochloric-boric acid mixture.*—Mix 500 cc of hydrochloric acid (sp. gr. 1.19) and 500 cc of water, add 20 g of pure boric acid, and warm until the boric acid has dissolved.

Dilute hydrochloric acid (1 : 5).—Mix 100 cc of hydrochloric acid (sp. gr. 1.19) and 500 cc of water.

Dilute hydrochloric acid (1 : 20).—Mix 50 cc of hydrochloric acid (sp. gr. 1.19) and 1,000 cc of water.

Dilute sulphuric acid (1 : 5).—Add 100 cc of sulphuric acid (sp. gr. 1.84) slowly and with stirring to 500 cc of water.

Sodium hydroxide-carbonate solution.—Dissolve 100 g of sodium hydroxide and 10 g of sodium carbonate in 1,000 cc of water.

Ammonium acetate solution (25 per cent).—Dissolve 250 g of ammonium acetate in 750 cc of water.

Stannous chloride solution.—Dissolve 50 g of the crystallized salt in 100 cc of hot concentrated hydrochloric acid and dilute to 1,000 cc.

Mercuric chloride solution.—Prepare a cold saturated solution.

Manganese solution.—(*a*) Dissolve 200 g of crystallized manganese sulphate in 1,000 cc of water. (*b*) Pour 400 cc of concentrated sulphuric acid slowly and with constant stirring into 1,300 cc of water and then add 300 cc of sirupy phosphoric acid (sp. gr. 1.71). Mix solutions (*a*) and (*b*).

Standard permanganate solution (approximately 0.03 N.)—Dissolve 1 g of potassium permanganate in distilled water, dilute to 1 liter, allow to stand for several weeks, filter through asbestos which is free from chlorides and organic matter, and standardize against the Bureau of Standards Standard Sample of Sodium Oxalate.

SOLUTION OF THE SAMPLE

Transfer 2.5 g of the pulverized rock to a 250 to 300 cc flask, add 50 cc of hydrochloric acid-boric acid mixture, and *boil* the solution gently in such a manner as to avoid concentrating the solution to less than half its original volume. The temperature of the solution during the boiling should be approximately 110° C., and it is desirable to use a flask with a long, narrow neck. If such a flask is not available, a funnel should be placed in the neck of the flask.

After boiling the sample of rock for one hour, dilute the solution to 100 cc and filter into a graduated 250 cc flask, washing the filter thoroughly with cold dilute hydrochloric acid (1 : 20). Cool the solution, dilute to the mark, and mix thoroughly.

DETERMINATION OF SOLUBLE ALUMINA

Transfer a 100 cc portion (representing 1 g of rock) of the prepared solution into a platinum dish and evaporate the solution nearly to dryness. Cool, add 15 cc of dilute sulphuric acid (1 : 5), and evaporate until copious fumes of sulphuric acid appear. Cool, dilute with about 100 cc of water, add 10 cc of concentrated hydrochloric acid, and heat until sulphates are in solution. If silica is present, filter and wash the filter thoroughly with dilute hydrochloric acid (1 : 20). Add several drops of a saturated solution of potassium permanganate and boil 10 minutes to oxidize any ferrous iron and organic matter.

Nearly neutralize the solution, which should have a volume of about 200 cc, with sodium hydroxide and pour it slowly and with constant stirring into 160 cc of a sodium hydroxide-carbonate solution. This may be done conveniently through a pipet. Transfer the solution and precipitate to a graduated 500 cc flask, cool, and dilute to the mark. Filter through a dry 12.5 cm No. 42 Whatman or similar paper, discard the first 10 to 20 cc, and then catch the filtrate in a 250 cc flask or graduate. In this procedure only a trace of calcium remains in solution.

Take exactly 250 cc of the filtrate, representing 0.5 g of the rock; acidify with hydrochloric acid, and add 10 cc of the concentrated acid in excess, and then 1 g of diammonium phosphate. Dilute to 500 cc and add macerated paper. The macerated paper prevents the gelatinous $AlPO_4$ from coagulating in lumps from which sodium salts and excess phosphate can not be washed.

Add 2 drops of methyl orange indicator, make just alkaline with ammonia, and restore the pink color with several drops of dilute hydrochloric acid (1 : 5). Heat the solution to boiling and add 30 cc of a 25 per cent solution of ammonium acetate. Continue the boiling for five minutes, filter on an 11 cm No. 42 Whatman or similar paper, and wash with hot 5 per cent ammonium nitrate solution until 5 cc of the washings gives an almost indistinguishable opalescence with an acidified solution of silver nitrate.

Dry the paper and precipitate by gentle heating in an open platinum or porcelain crucible, burn the carbon at a low temperature, and finally cover and ignite at about 1,000° C. to constant weight. Weigh as $AlPO_4$ and multiply by 0.418 to obtain the weight of Al_2O_3.

Unless the reagents are known to be free from aluminum, a "blank" run should be carried through all steps of the method.

DETERMINATION OF SOLUBLE IRON

Transfer a 100 cc portion (representing 1 g of rock) of the prepared solution to a 250 cc beaker. If only a small quantity of organic matter is present, as is usually the case, add 1 to 2 cc of a saturated solution of potassium permanganate and then boil to expel chlorine. In the rare event of much organic matter, add a few crystals of potassium chlorate at intervals as the solution is evaporated to dryness and redissolve the residue in 30 cc of dilute hydrochloric acid (1 : 5).

Heat the solution to boiling and reduce with a small excess of stannous chloride, added dropwise while agitating the solution. Wash the sides of the beaker with distilled water and cool rapidly. Add 10 cc of mercuric chloride solution and stir vigorously for one minute. Pour the mixture into a large porcelain casserole containing 20 cc of the manganese solution in about 500 cc of water that has been faintly tinted with permanganate solution. Titrate with 0.03 *N* permanganate solution to the original tint, and correct the result by the volume of permanganate required for a titration of the reagents alone.

DETERMINATION OF TOTAL FERRIC OXIDE, ALUMINA, LIME, AND MAGNESIA

PREPARATION OF THE SOLUTION

Transfer 2.5 g of the rock to a platinum dish (on account of the fluorides present) and digest for 15 to 30 minutes on the steam bath, with 50 cc of dilute hydrochloric acid (1 : 1). Remove any insoluble matter by filtration, ignite in platinum, fuse with a small quantity of sodium carbonate, take up the melt in dilute hydrochloric acid, and add the solution to the filtrate. Remove the silica by two evaporations in platinum with hydrochloric acid and intervening filtration. If considerable quantities of fluorides are present, dust a little powdered silica (free from iron, aluminum, calcium, and magnesium) into the solution from time to time during the evaporation with hydrochloric acid. Ignite the silica and treat it with sulphuric and hydrofluoric acids. If any residue remains, fuse it with a little sodium carbonate, dissolve the melt in a small quantity of dilute hydrochloric acid, and add the solution to the main filtrate. Dilute the solution to exactly 250 cc, mix thoroughly, and pipet 50 cc aliquot portions, each representing 0.5 g of sample, into beakers for determinations of (1) total ferric oxide, (2) lime and magnesia, and into platinum dishes for the determination of (3) total alumina.

TOTAL FERRIC OXIDE

Total ferric oxide is conveniently determined in one aliquot portion by the method which is given for "Soluble iron" after provision has been made for any platinum introduced through the solution treatment. Platinum interferes in permanganate titrations that are made after reductions with stannous chloride and causes high results. If platinum is removed by precipitation with hydrogen sulphide, another difficulty arises through the formation of polythionic compounds which also react with permanganate and cause high values. The latter are removed by boiling to expel hydrogen sulphide and then continuing the boiling as 2 cc of a 5 per cent solution of permanganate is added.

TOTAL ALUMINA

Total alumina is satisfactorily determined in another aliquot portion of the complete solution by the method given for "soluble alumina," provided a double precipitation of the aluminum as phosphate is made. In the first precipitation macerated paper can be omitted, and the washing of the precipitate need be only very slight. The error introduced by the volume of the sodium hydroxide precipitate is negligible. To confirm the result for alumina, the aluminum phosphate can be dissolved and its P_2O_5 content carefully determined and then subtracted from the weight of $AlPO_4$.

TOTAL LIME

To a third aliquot portion of the solution add sufficient hydrochloric acid to make a total of 10 cc of concentrated hydrochloric acid in the solution. He to about 50° C., add several drops of methyl oran neutralize with ammonium hydroxide, and add 1 cc of dilute ammonium hydroxide (sp. gr. 0.96) in excess. Just acidify the solution with oxalic acid (10 per cent solution) and then add 10 cc in excess. Heat the solution to boiling, stir vigorously, and allow to boil one to two minutes. It is necessary to boil and to stir vigorously after the addition of oxalic acid in order to free the calcium oxalate precipitate from iron, aluminum, etc., which may at first be thrown down in part.

Add 50 cc of a saturated solution of ammonium oxalate (about a 4 per cent solution), dilute to 200 cc with hot water, boil for one minute, and place on the steam bath for one hour. Cool to room temperature, filter, and wash several times with cold ammonium oxalate-oxalic acid wash solution (2 g $(NH_4)_2C_2O_4$ and 1 g $H_2C_2O_4 \cdot 2H_2O$ per 1,000 cc of water). Reserve the filtrate for the determination of magnesia.

Ignite the precipitate in platinum, dissolve in 40 cc of dilute hydrochloric acid (1 : 5), and filter if any silica separates. Dilute to 200 to 250 cc, add 0.01 g of $FeCl_3$, make slightly ammoniacal, and add 10 cc of bromine water. Digest at a temperature a little below the boiling point for 15 minutes and then add 5 cc more of bromine water. Allow to stand on the steam bath for one-half to one hour, filter, and wash thoroughly with hot ammonia-ammonium chloride wash solution (10 cc of strong ammonium hydroxide and 10 g of ammonium chloride per liter). Acidify the filtrate with hydrochloric acid, add 25 cc of saturated solution of ammonium oxalate, heat nearly to boiling, and then make ammoniacal, adding about 1 cc of strong ammonium hydroxide in excess. Boil for one to two minutes, allow to stand on the steam bath for one hour, cool to room temperature, filter, and wash with a cold 1.0 per cent solution of ammonium oxalate.

Ignite the precipitate, and weigh as CaO in a covered crucible. Repeat the ignition and weighing until constant weight is obtained.

MAGNESIA

Combine the two filtrates from the calcium determination, slightly acidify, concentrate to a volume of 300 cc, add 2 to 3 g of diammonium phosphate, and 3 g of citric acid, and make slightly ammoniacal. Stir vigorously for a few minutes, add 25 cc of ammonium hydroxide (sp. gr. 0.90) and allow to stand in a cool place overnight. Filter, wash the precipitate a few times with dilute ammonium hydroxide (5 per cent by volume) and redissolve it in 50 cc of warm dilute hydrochloric acid (1 : 5). Add 0.1 to 0.2 g of diammonium phosphate and reprecipitate by adding ammonium hydroxide dropwise and with constant stirring. Finally add 5 cc of ammonium hydroxide (sp. gr. 0.90) in excess and let stand for at least four hours. Filter, wash, ignite and weigh the precipitate as directed under the gravimetric method for phosphoric acid.

For a full discussion of the methods used in the analysis of this phosphate rock, see The Analysis Phosphate Rock, by G. E. F. Lundell and J. I. Honman, Journal of the Association of Official Agricultural Chemists, Vol. III, No. 2, p. 184, Nov. 1924.

U. S. GOVERNMENT PRINTING OFFICE: 1927 J51026